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HETA 94-0353-2629
USDA Plant Inspection and Quarantine Station
Miami, Florida

Max Kiefer

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Max Kiefer of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Ms. Ladina Saluz, Steve Lenhart, and John Decker. Desktop publishing by Ellen Blythe and Pat Lovell.

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USDA Plant Inspection and Quarantine Station
Miami, Florida
February 1997

Max Kiefer, CIH

SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at the USDA Plant Inspection and Quarantine Station (PIQS) in Miami, Florida. The primary health concern of the requesters was employee handling of plant material that may have been treated with pesticides. The requesters asked NIOSH to evaluate USDA employee exposure to pesticides on imported plants.

In response to this HHE request, additional information about imported plants (type of plants, countries of origin) was obtained to determine what pesticides may have been applied prior to export to the United States. This entailed conducting literature reviews and requesting information from ornamental plant brokerage firms in south Florida. Methods for sampling and analyzing the surfaces of leaves for unknown pesticides (dislodgeable residue) were identified, developed, and evaluated. In February 1995, different leaf sampling techniques were field-tested at a greenhouse to determine an optimum method for sampling dislodgeable residue.

NIOSH investigators conducted an initial site visit at the PIQS facility on June 13-15, 1995. The objectives of this visit were to observe the plant inspection process, obtain samples from imported plants, conduct personal monitoring to assess potential skin exposures to pesticides, and collect area air samples for pesticides identified on the leaf samples. Two techniques for foliage sampling were used during this survey: (1) collection of leaf tissue using a leaf punch with a standardized sample size, and (2) wipe samples of leaves using cotton gauze moistened with isopropyl alcohol. Skin exposures were assessed using cotton glove monitors worn by workers during inspections. During this site visit, plant inspection activity was slower than normal, and only a few plant inspections were conducted. Thirteen leaf samples and 15 matching gauze wipe samples were obtained. Fourteen pairs of glove samples were collected and, based on the results of the leaf sampling, six pairs of gloves were analyzed.

On May 7-8, 1996, a follow-up site visit was conducted to collect additional samples. During this site visit, foliage sampling was conducted using only the wipe sampling technique (this was determined to be the optimum method based on field-testing conducted in February 1995 and during the previous site visit). Twenty-nine gauze wipe samples were collected and analyzed during this site visit. Skin exposure was assessed using cotton glove monitors, and area air samples were collected. Sixteen pairs of glove samples were collected and, based on the leaf sampling results, fourteen pairs of gloves were analyzed. Five area air samples were collected, including one sample obtained inside a truck bed containing plants from El Salvador. This site visit was conducted in conjunction with a similar NIOSH project at the Miami USDA Animal and Plant Health Inspection Service (APHIS) Cargo and Maritime commodity inspection group (HETA 96-0083-2628). Inspection activity was much higher during this follow-up visit and a greater number of samples were obtained.

The dislodgeable residue samples were analyzed for 58 pesticides using several analytical techniques. Cotton gloves worn by inspectors and the area air samples were analyzed for compounds detected on the foliage samples.

During the first site visit, five different pesticide residues were detected on five gauze and five leaf punch samples. The fungicide benomyl and the carbamate insecticide aldicarb were the most commonly detected pesticides. Six pairs of glove samples were analyzed for these two pesticides. Benomyl was detected on 8 of the 12 gloves. No aldicarb was detected on any of the gloves. Four air samples were analyzed for the organo-phosphate pesticide monocrotophos; monocrotophos was not detected on any of the samples.

During the May 7–8, 1996, site visit, pesticide residue(s) were detected on 19 (66%) of the gauze wipe samples. Twenty-one different insecticides and fungicides were identified. The fungicide captan was found on 11 samples, more than any other compound. The detected residues encompassed several classes of compounds, including organophosphate, carbamate, pyrethrin, and organo-chlorine. Pesticide residue was detected on 10/14 (71%) glove pairs analyzed. The air samples were analyzed for tetradifon, chlorpyrifos, diazinon, malathion, methamidophos, and profenofos. All results were below the analytical limit of detection for the analytes.

The pesticides detected on the foliage samples were ranked using the Environmental Protection Agency toxicity classification system for pesticides. This system categorizes pesticides into four toxicity classes, from highest (category I) to lowest (category IV). Twelve of the 21 compounds detected were toxicity category I pesticides. The number of compounds in each category decreased from the highest to lowest toxicity ranking, with only one toxicity category IV compound detected.

The use of protective gloves was not uniform among employees as some workers were observed not wearing gloves during inspections. An inspectors decision to wear gloves during an inspection seemed to be based on the presence of visible residue on the plants, or an unusual odor when a plant container is opened. The results of this HHE indicate that visible residue on plant material is not a good indicator of whether pesticides are present.

The results of this HHE indicate USDA PIQS plant inspectors are at risk for skin exposure to pesticides during the handling of imported plants. Pesticide residues were detected on the majority of the foliage samples collected, and 21 different pesticides were found. Measurable quantities of pesticides were found on cotton glove monitors worn by plant inspectors. No measurable pesticides were found on any air samples. The cotton glove monitors were worn over the inspectors vinyl or latex glove (when worn) and these results only provide information on the potential for exposure if protective gloves were not worn. The efficacy of the disposable gloves to prevent contact with pesticide residues was not evaluated during this project. The majority of the compounds found on the foliage samples are considered to be highly toxic pesticides, with only one of the detected pesticides in the lowest toxicity ranking. The presence of visible residue on plant material was not a good indicator that a pesticide would be detected. Chemical-resistant gloves should always be worn by PIQS inspectors when handling imported plants. Suggestions for reducing potential exposures are in the Recommendations section of this report.

Keywords: SIC 9641 (Regulation of Agricultural Marketing and Commodities). Pesticide Residue, Plant Inspection, Ornamental Plant Imports, Skin Exposure, Leaf Sampling.

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INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) received a management request from the United States Department of Agriculture (USDA) Plant Inspection and Quarantine Service (PIQS) in Miami, Florida, to evaluate the potential for worker exposure to pesticides during inspections of imported plants. No reported health complaints were received with the request.

NIOSH investigators conducted site visits at the Miami PIQS facility on June 14–15, 1995, and May 7–8, 1996. Prior to the site visits, information was solicited to identify the pesticides that may have been applied to plants in the host countries. Analytical methods for measuring pesticide residues on foliage were also developed and refined. During each site visit, foliage and air samples were collected, and the potential for skin exposure was assessed using glove monitors. Work practices during the plant inspection process were observed.

A letter describing preliminary findings and recommendations was provided to PIQS management on September 20, 1995.

BACKGROUND

Process Description

The USDA PIQS is located at the Miami International Airport and began operation in 1947. Thirteen employees work at the PIQS, including 5 inspectors, 4 specialists (e.g., entomology, plant pathology), maintenance, and administration. Some inspectors are represented by the National Association of Agricultural Employees (NAAE), Local #8. The PIQS is one of three USDA groups in Miami responsible for inspecting imported plants and plant products. The other two groups are Cargo (cut flowers and produce) and Maritime (produce). Approximately 80% of imported propagation material (e.g., live ornamental plants such as orchids, palms, etc.) entering the United States is inspected at the Miami Station. The objectives of an inspection

are to ensure that imported plants are free of disease and infestation (microbiological, insect, and noxious weed), and are not an endangered or threatened species. Plants are received from many South American and Caribbean countries, as well as from the Far East and Europe. Exporters are not required to label or provide information about whether a plant shipment has been treated with a pesticide.

When imported plants arrive in the U.S.A., customs personnel issue a provisional release to the importers on the condition that the plants are approved by the USDA. The import brokers then bring samples of each type of plant material to the PIQS for inspection. The plants are typically in boxes, and shipment sizes may range from 20 to 200 boxes per shipment. For each shipment, the number of boxes inspected and the scope of the inspection is based on the type of plant and historical experience with the exporter. In general, there is considerable handling of the plants, and close visual evaluation using magnifying glasses and, occasionally, microscopy. If the plants pass inspection, PIQS inspectors release them to the importer for distribution throughout the U.S.A. The standard inspection service is operated from 8 a.m.-4:30 p.m., Monday through Friday. However, because of the perishable nature of some imported material, service is available 24 hours per day, and Saturday is considered to be one of the busiest days. The duration of an inspection ranges from 10 minutes to 1 hour per shipment. Daily logs are kept noting the size of a shipment, plant type, country of origin, and the name of the exporting grower or firm.

In addition to imported plant material, the PIQS is also responsible for inspecting U.S.-grown plants and produce destined for export, as well as re-exported material (e.g., imported to the U.S. and subsequently exported to another country). Approximately 40% of inspected commodities are either export or re-export material.

If a shipment does not pass inspection (insect infestation or plant disease is detected), a broker has the option of returning the entire shipment to its country of origin or destroying the plants in a

gas-fired incinerator located behind the PIQS facility. Occasionally, infested or diseased products are treated on-site in one of three methyl bromide fumigation chambers by PIQS personnel. All PIQS inspectors are Certified Pesticide Applicators.

PIQS Pesticide Residue Concerns

Although no illnesses among PIQS inspectors have been reported, there have been complaints of odors and visible residue on some plant shipments. In some cases, spent aerosol cans of pesticides used to fog the plants have been found inside the shipping containers or vehicle trailers. Based on experience with certain suppliers, countries, or types of plants, PIQS inspectors can often predict when they may encounter pesticide residues. For example, orchids have a "reputation" of being heavily treated with pesticides, and certain ferns are often dipped in pesticides and wrapped while still wet prior to shipment. Occasionally, in an effort to reduce the potential for exposure, PIQS inspectors may elect to conduct an inspection outside. PIQS management has a form letter that is issued to plant brokers whenever shipments are received for inspection that appear to be heavily contaminated with pesticides. The letter warns the broker that future shipments found to be in similar condition will be refused entry.

Disposable latex and vinyl gloves are available for use, and most inspectors use them during inspections. The gloves are typically discarded after each inspection. Respiratory protection or special clothing is not worn during routine plant inspections.

METHODS

Foliage Residue Sampling and Analysis

To evaluate dislodgeable pesticide residues on imported plants, a necessary first step was determining the agricultural chemicals that may have been applied. Measuring a known material is more analytically feasible (the specific method for a compound can be selected) than trying to identify and quantify an unknown substance. This is particularly true for pesticides, which encompass a wide variety of chemical classes and are often very complex compounds. To obtain this information, the literature was researched for similar studies that may have been conducted. Information on grower application practices in host countries was also requested from plant brokerage firms in south Florida. Existing sampling and analytical methods for assessing pesticides on foliage were identified and reviewed.^(1,2,3,4) To determine the optimum method, two techniques (leaf punch and leaf wipe) for sample collection and analysis were field tested in February 1995, at a greenhouse where applications of known pesticides had occurred. The sampling and analytical methodology was further refined after the June 1995 survey. Efforts to obtain application information from major plant brokerage firms were unsuccessful, as the importing brokers generally did not know what pesticides were applied by the off-shore growers. Appendix A provides details on the analytical methodology used for measuring pesticide residues on plant surfaces.

Because techniques for assessing foliar surfaces for a broad array of potential pesticides in multiple chemical classes were not available, a list of 15 pesticides considered most likely to be present, and of higher concern from a toxicological standpoint, was developed. This list provided a baseline for analysis of the foliage samples. This list (Appendix B) was based on high volume usage in Central America, recommended use by the ornamental industry, and toxicity. The pesticide list contained compounds from several chemical classes

(organophosphate, organochlorine, pyrethroid, carbamate). For some classes of pesticides, the method was conducive to measuring additional compounds within that chemical class (e.g., organophosphate, organochlorine), and the samples were analyzed for additional pesticides beyond the list of 15. A complete list of the pesticides measured on the foliar samples is presented in Appendix A.

June 14–15, 1995, Site Visit

Dislodgeable Residue Sampling

Samples were collected from the leaves of imported plants via two sampling methods: (1) a leaf punch (circular area of 1.25 or 5.0 square centimeters) was used to collect 5 leaf punches per sample from each plant shipment, and (2) a companion sample from each plant shipment was obtained using 3" X 3" pre-extracted cotton gauze moistened with 95% isopropyl alcohol (unknown surface area). To prevent cross-contamination, NIOSH investigators wore a new pair of disposable latex gloves for each sample collected. For the gauze samples, both sides of 5 plant leaves were wiped using firm pressure. In some cases the flower or stalk (e.g., Dracena or corn plant) of the plant had to be wiped. When possible, two or more samples were collected from each commodity shipment. The leaf samples were obtained using a Birkestrand Precision Sampler Punch that allows a sample collection jar to be attached directly to the punch.⁴ No surfactant or solution was added to the leaf punch samples. The punch cutting area was cleaned between sample collections. For each sample, the plant type, country of origin, presence of any visible residue or odor, and any shipping notations of pesticide applications were recorded. Samples were placed in labeled amber jars and stored in a freezer prior to shipment, and were shipped cold via overnight express to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis. Fifteen gauze wipes and 13 leaf samples were collected. Blank gauze wipes were submitted with the samples. Each sample was analyzed for the presence of 58 pesticides (Appendix A).

Skin Exposure Assessment

Thirty-one pre-extracted sampling glove monitors made of 100% cotton were used to assess the potential for skin contact with pesticides during a plant inspection. For those workers using disposable protective gloves during plant inspections, the sample glove monitors were worn **over** the worker's disposable gloves. A different set of glove monitors were used for each batch of plant material inspected. Sampling duration, name and country of origin of the inspected material, and the presence of unusual odor or residue were recorded for each sample set. After sampling, glove monitors were placed in labeled amber jars and sealed with teflon®-lined caps. NIOSH investigators wore protective gloves when removing the sampling glove monitors. Left- and right-hand gloves were placed in separate jars for each test subject and stored in a freezer until shipment. The samples and field blanks were then shipped via overnight delivery to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis. All glove monitors were placed on hold until after the foliage sampling results were available, and were analyzed for pesticides identified on the leaf samples. Appendix A provides details on the analytical methods used for the glove samples.

Air Monitoring

During the June 1995 site visit, eight area air samples were collected for analysis of organo-phosphate pesticides detected on the leaf or wipe samples. All samples were placed on hold until after the foliage samples had been analyzed. Calibrated air sampling pumps were located above the inspection tables and connected via tygon® tubing to collection media. Monitoring was conducted for the duration of the workday. After sample collection, the pumps were post-calibrated and the samples stored in a freezer until shipment. The samples were submitted by overnight delivery to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis. Field and media blanks were submitted with the samples.

The air samples were collected using OVS-2 (QSHA

Versatile Sampler) sorbent tubes at a flow rate of 1 liter per minute. The samples were desorbed and analyzed according to NIOSH fourth edition analytical method 5600.⁽⁵⁾ The sampling and analytical technique is specific for organo-phosphate pesticides.

May 7–8, 1996. Site Visit

Dislodgeable Residue Sampling

Based on the results of the February 1995 leaf sampling field evaluation, and the June 1995 site visit, wipe sampling with pre-extracted 3" X 3" cotton gauze moistened with technical grade (99%) isopropyl alcohol (IPA) was determined to be the optimum sample collection method. The wipe samples provided greater sensitivity and allowed for the analysis of more compounds than the leaf-punch method. A disadvantage of the wipe sampling technique is that the area sampled could not be standardized, only approximated. As such, quantifiable results (amount of residue per leaf area), which would allow for comparison among foliar samples, are not easily obtainable. For the purposes of this study, however, sensitivity was a more important factor, as only qualitative data from the leaf sampling was necessary to make a decision about which gloves to analyze.

Twenty-nine gauze wipe samples were collected during this site visit. Sample collection and handling methods were the same as those used during the June 14–15, 1995, survey except that 99% IPA was used instead of 95% IPA. For each sample, the plant type, country of origin, presence of any visible residue or odor, and any shipping notations of pesticide applications were recorded. Samples were placed in labeled amber jars and stored in a freezer prior to shipment, and were shipped cold via overnight express to the NIOSH contract laboratory for analysis. Blank gauze wipes were submitted with the samples. Each sample was analyzed for the presence of 58 separate pesticides (Appendix A).

During the analysis, additional compounds were suspected to be present on some of the gauze wipe

samples. For these samples, an additional analytical step entailing gas chromatography–mass spectroscopy detection (GC–MSD), was used to identify additional pesticides.

Skin Exposure Assessment

Based on the results of recovery studies conducted by the NIOSH contract laboratory, pre-extracted 65% polyester and 35% cotton gloves were used for this survey instead of 100% cotton gloves. Sixteen glove pairs (32 gloves) were used to assess the potential for skin contact to various pesticides during the plant inspection process. As with the June 1995 site visit, for those workers using disposable protective gloves during plant inspections, the sample glove monitors were worn **over** the worker's disposable gloves. A different set of glove monitors were used for each batch of plant material inspected. Sampling duration, plant name and country of origin, and the presence of unusual odor or residue were recorded for each sample set. After sampling, the glove monitors were placed in labeled amber jars and sealed with teflon®-lined caps. NIOSH investigators wore protective gloves to remove the sampling glove monitors. Left- and right-hand gloves were placed in separate jars for each test subject and stored in a freezer until shipment. The samples and field blanks were then shipped via overnight delivery to the NIOSH contract laboratory for analysis. The glove monitors were placed on hold until after the foliage sample results were available, and were analyzed for pesticides identified on the leaf samples.

Air Monitoring

Four area air samples for organo-phosphate pesticides were collected inside the PIQS facility. The samples were placed on hold until after the foliage samples had been analyzed. Calibrated air sampling pumps were located over the inspection tables and connected via tubing to collection media. Monitoring was conducted for the duration of the workday on both May 7 and May 8. On May 7, an 80-minute area sample was collected inside the trailer of a delivery truck carrying Dracena (corn plant) from El-Salvador. After the samples were

collected, the pumps were post-calibrated and the samples stored in a freezer until shipment. The samples were submitted by overnight delivery to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis. Field and media blanks were submitted with the samples. The samples were placed on hold until after the foliage samples were analyzed.

The air samples were collected using OVS-2 (OSHA Versatile Sampler) sorbent tubes at a flow rate of 1 liter per minute. The samples were desorbed and analyzed according to NIOSH fourth edition analytical method 5600.⁽⁵⁾

EVALUATION CRITERIA

General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),⁽⁶⁾ (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVsTM),⁽⁷⁾ and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).⁽⁸⁾ In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

Skin Exposure

Exposure standards, guidelines, or recommendations by NIOSH or regulatory agencies have not been established for the concentration of the pesticides monitored on skin or work clothes. However, skin

exposure to pesticides is often considered to be a more important portion of total exposure than inhalation.^(9,10,11) Pesticide applications generally entail considerable contact during mixing, spraying, and handling of treated crops. Loosely bound residues on plant material can be a major source of exposure for workers.^(4,12) In general, hand exposures represent a major fraction of total dermal exposure.⁽¹³⁾ Evaluation of the amount of material potentially available for absorption can provide estimates of skin exposure. Additionally, these types of assessments are useful for evaluating the need for and efficacy of control measures, as well as personal protective equipment. In some cases, where there is information on skin permeability and there is inhalation and biological monitoring data, skin contact assessments can theoretically provide more quantitative information on absorption or dose via the skin route. There are numerous techniques available to estimate the potential for skin contact, including absorbent patches and analysis of hand rinses. However, there is no standard protocol for the assessment of the degree of skin contact or the interpretation of data.⁽¹⁴⁾

Pesticides

A pesticide is any substance or mixture intended to prevent, destroy, repel, or mitigate insects (insecticide, miticide, acaricide), rodents (rodenticide), nematodes (nematocide), fungi (fungicide), or weeds (herbicide), designated to be “pests.” For each type of pesticide there are numerous modes of action, chemical classes, target organs, formulations, and physicochemical properties. Pesticide toxicity is equally diverse, and even within a similar chemical class, individual compounds ranging from extremely toxic to practically nontoxic can be found.⁽¹⁵⁾ As such, generalizations about the toxicity of pesticides cannot be made without considerable qualification and explanation. In the United States, regulatory responsibility to protect public health and the environment from the risks posed by pesticides lies with the Environmental Protection Agency (EPA) Office of Pesticide Programs. Currently, there are

620 active ingredients (AI)* in approximately 20,000 EPA registered pesticide products.⁽¹⁶⁾ In the United States alone, over one billion tons of pesticide products are used each year.⁽¹⁶⁾

Organophosphate Pesticides

A variety of organophosphate chemicals are commonly used as insecticides because they are biodegradable as well as effective. Organophosphate chemicals, however, can cause adverse health effects in exposed humans through the inhibition of cholinesterase (ChE) enzymes. Symptoms after exposure to organophosphate chemicals usually appear quickly, often within a few minutes to two or three hours.⁽¹⁵⁾

Organophosphate insecticides typically cause illnesses in humans by binding to and inhibiting acetylcholinesterase (A-ChE) at nerve endings. A-ChE is a ChE enzyme that metabolizes, and thus controls, the amount of acetylcholine (nerve impulse transmitter) available for transmitting nerve impulses. Inhibition of A-ChE causes acetylcholine to accumulate at nerve endings, resulting in increased and continued acetylcholine stimulation at those sites. Symptoms of A-ChE inhibition include the following:

The organophosphate-ChE bond is stable and largely irreversible, so recovery of ChE activity depends on the generation of new ChE. ChE inhibition, therefore, can sometimes last for months.

ChE inhibition can be measured as decreases in ChE activity. Red blood cell cholinesterase (RBC-ChE), like ChE in nerve tissues, is an A-ChE. Its rate of regeneration nearly parallels that of A-ChE in nerve tissues, making its measurement a useful method of biologically monitoring exposure to organophosphate insecticides. A significant decrease in RBC-ChE activity indicates either a recent excessive exposure

*Active Ingredient is the material, or component, present in a pesticide formulation responsible for killing or controlling the target pest. Pesticides are regulated primarily on the basis of active ingredients, often expressed in terms of percent, pounds per gallon, etc.

or repeated exposures to amounts sufficient to depress ChE activity before recovery is complete. Other types of cholinesterase, such as plasma cholinesterase or pseudocholin-esterase (P-ChE), are more sensitive to organophosphate inhibition. P-ChE activity, however, returns to baseline values earlier than RBC-ChE activity. Therefore, P-ChE values may not reflect the severity of toxicity unless blood specimens are obtained soon after exposure. P-ChE activity can also be affected by factors unrelated to organophosphate exposure, including medical conditions such as liver disease.⁽¹⁷⁾ P-ChE activity is clinically useful in monitoring cases of severe organophosphate poisoning, but its use in monitoring workplace exposures is limited.

The range of toxicity and potential health hazard varies widely among organophosphate pesticides. The hazard associated with each is also dependent on other factors, including frequency of use, concentration, formulation, physical and chemical

Carbamate Pesticides

Exposure to carbamate insecticides can also cause ChE inhibition and its related symptoms. Unlike the organophosphate-ChE bond, however, the carbamate-ChE bond is rapidly broken, and carbamates are considered to be reversible ChE inhibitors. As such, the effects of carbamate exposure last for a much shorter time than that of organophosphate exposure. For this reason, biological monitoring of RBC-ChE activity may not necessarily reflect exposure to carbamate insecticides, and there is a greater span between the dose that will produce symptoms and the lethal dose.⁽¹⁵⁾ As with the organophosphates, there is a wide range of acute toxicities among the carbamates. Unlike the organophosphates, however, most carbamates have low dermal toxicity and are only slightly absorbed through the skin (a notable exception to this is the pesticide aldicarb [Temik®]).^(15,18)

Synthetic Pyrethroid Pesticides

Synthetic pyrethroid insecticides are chemically similar to natural pyrethrins. Pyrethrins are the active insecticidal ingredient in pyrethrum, which is the extract of chrysanthemum flowers and one of the oldest insecticides known to man.^(15,18) Synthetic pyrethroids have been modified to increase their stability in the natural environment, and make them suitable for use in agriculture.

Certain pyrethroids have been shown to be highly neurotoxic in laboratory animals when administered intravenously or orally.⁽¹⁸⁾ Systemic toxicity by inhalation or dermal absorption is low, and there have been very few reports of human poisonings by pyrethroids. Very high absorbed doses could result in incoordination, tremor, salivation, vomiting, and convulsions.⁽¹⁸⁾ Some pyrethroids have caused sensations described as stinging, burning, itching, and tingling — with progression to numbness, when contact with the skin occurs. Sweating and exposure to the sun can enhance this discomfort. Pyrethroids are not cholinesterase inhibitors.

Organochlorine Pesticides

Because of their persistence in the environment and biologic media, the use of many organochlorines such as DDT, dieldrin, mirex, and chlordane have been banned or sharply curtailed in the United States. The major toxic action of organochlorine pesticides is on the nervous system which, in cases of severe poisoning, can manifest as convulsions and seizures.⁽¹⁸⁾ Early signs of poisoning may include headache, dizziness, nausea, vomiting, and mental confusion. Following exposure to some organochlorine pesticides, a large part of the absorbed dose may be stored as the unchanged parent compound in fat tissue. As a class of compounds, organochlorine pesticides are often considered less acutely toxic, but with a greater potential for chronic toxicity, than the organo-phosphate or carbamate pesticides.⁽¹⁵⁾ As with the other pesticide classes, however, there is a wide range of acute toxicities of individual organochlorine compounds. Organochlorine pesticides are not cholinesterase inhibitors.

RESULTS AND DISCUSSION

PIQS employees were aware of the potential for exposure to residual agricultural chemicals on imported plants and the need to take precautions. However, the use of gloves was not uniform among employees as some workers were observed not wearing gloves during inspections. An inspector's decision to wear gloves seems to be based on the presence of visible residue on the plants, or an unusual odor when the plant container is opened. Although these are prudent measures, pesticide contamination can still be present without odor or visible residue, and the senses should not be used for determining whether precautions should be taken.

June 14–15, 1995, Survey

The results of the dislodgeable foliar residue sampling are shown in Tables 1 and 2. Inspection activity was less than normal during this survey and only a few shipments were evaluated. Thirteen leaf samples and 15 matching gauze wipe samples were submitted for analysis. Pesticide residues were detected on 5 gauze and 5 leaf punch samples (Figure 1). For three of the six pairs of samples (leaf and gauze wipe) where one of the sample methods detected a contaminant, the matching sample also detected the same contaminant. Five different pesticides were detected on the samples. The fungicide benomyl and the carbamate insecticide aldicarb were the most commonly detected pesticides.

Figure 2 shows the compounds detected by country of origin. Residue was detected on three of the six samples collected from Thailand (more samples were collected from this country than any other). All of the samples collected from Thailand were orchids. As noted in Table 1, the presence of visible residue on plant material was not a good indicator that a pesticide would be detected. No unusual odors were reported from any of the plant inspections monitored.

Fourteen sets of glove samples (28 gloves) were

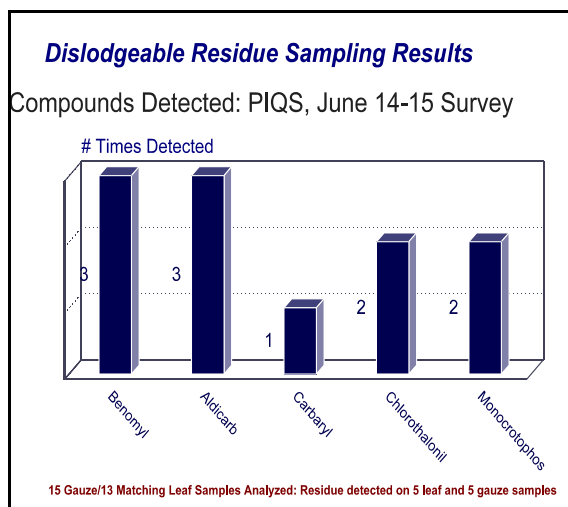


Figure 1

collected. Based on the results of the leaf sampling, six sets of gloves (12 gloves) were analyzed and the results are shown in Table 3. All of the glove samples were obtained during the inspection of wild harvest bromeliads from Guatemala. There were no matching glove samples from the foliar samples collected on June 14, as these plants had already been inspected prior to the NIOSH site visit. Although foliar samples were obtained, glove monitoring during the inspection of these plants was not conducted.

The six sets of glove samples (12 gloves) analyzed corresponded to gauze and leaf samples that detected aldicarb and benomyl. Benomyl was detected on 8 of the 12 gloves (67%, LOD = 20 µg/sample). No aldicarb was detected (LOD = 40 µg/sample) on any of the gloves.

Monocrotophos was the only organo-phosphate

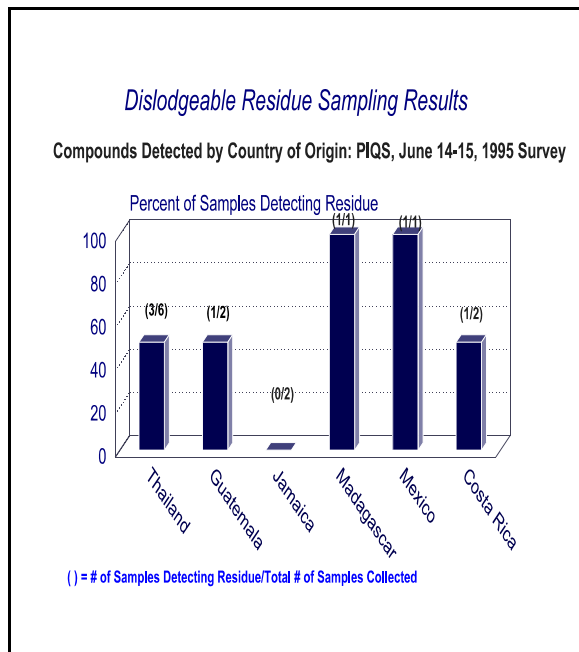


Figure 2

pesticide detected on the wipe/leaf samples collected on June 14. No monocrotophos was detected on any of the OVS-2 area air samples collected on June 14.

May 7–8, 1996, Survey

Twenty-nine gauze wipe samples were collected and analyzed during this site visit. The results are shown in Tables 4 and 5. Inspection activity during this site visit was higher than during the June 1995 survey, and more samples were collected.

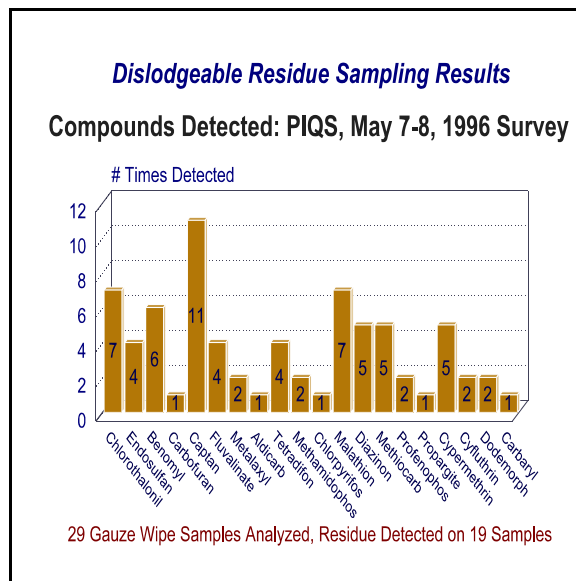


Figure 3

Pesticide residue(s) were detected on 19 (66%) of the gauze wipe samples. Twenty-one different insecticides and fungicides were detected on the gauze wipe samples (Figure 3). The fungicide captan was found on 11 samples, more than any other compound (Figure 3). The detected residues encompassed several classes of compounds, including organophosphate, carbamate, pyrethrin, and organo-chlorine (Table 8).

Figure 4 shows the compounds detected by country of origin, and the percent of the samples from each country where pesticide residue was detected. As with the June 1995 survey, more samples (14) were collected from shipments from Thailand than any other country, followed by El-Salvador (3), Belize (3), and Costa Rica (3). Residues were detected on 7 (50%) of the samples from Thailand, and on all of the samples from El-Salvador and Belize and other countries.

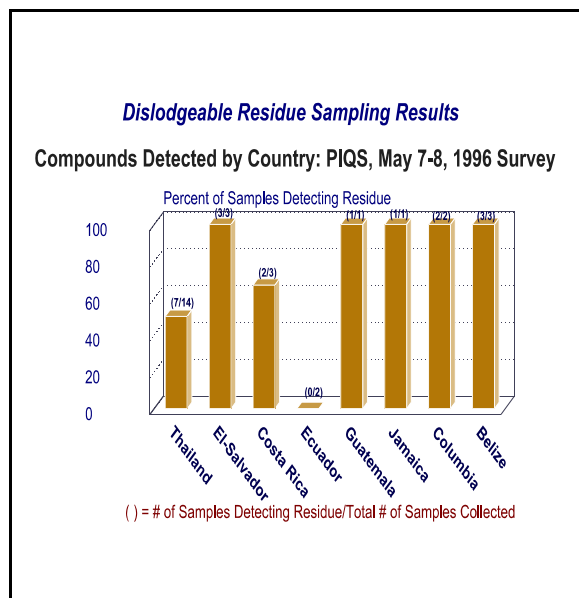


Figure 4

Figure 5 summarizes the dislodgeable residue sampling results and provides information on the number of compounds detected per sample by country of origin. For example, an average of

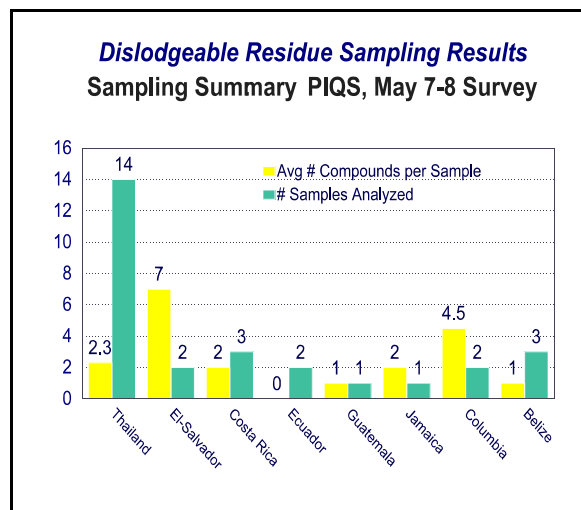


Figure 5

2.3 compounds per sample were detected on the 14 samples collected from plants imported from Thailand (a total of 32 compounds were detected) and 7 pesticides per sample were detected on the 2 samples from plants imported from El-Salvador (a total of 14 compounds).

Figure 6 categorizes the compounds detected by toxicity, based on the Environmental Protection Agency (EPA) toxicity classification method for pesticides. The EPA requires pesticides to be classified and labeled using signal words determined by the pesticides' level of toxicity. Toxicity is based on oral, inhalation, dermal, eye, or skin effects, with categories ranging from I – IV. Pesticides in toxicity category I are considered the most toxic, and require the signal words **Danger** or **Poison** (if the classification is based on oral, inhalation, or dermal toxicity). Toxicity category IV pesticides are the least toxic and are required (along with category III pesticides) to be labeled with the signal word **Caution**. Toxicity category II pesticides use the signal word **Warning**.

As shown in Figure 6, 12 of the 21 compounds detected were toxicity category I pesticides. The number of compounds detected in each category decreased from the highest to lowest toxicity ranking, with only one toxicity category IV compound detected (benomyl). Table 8 shows the toxicity category for each compound detected.

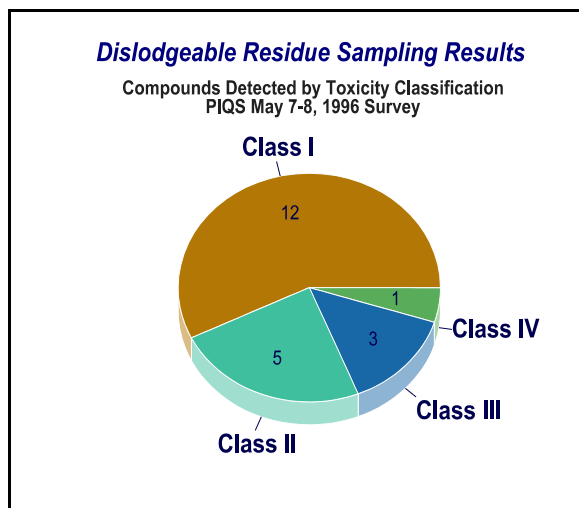


Figure 6

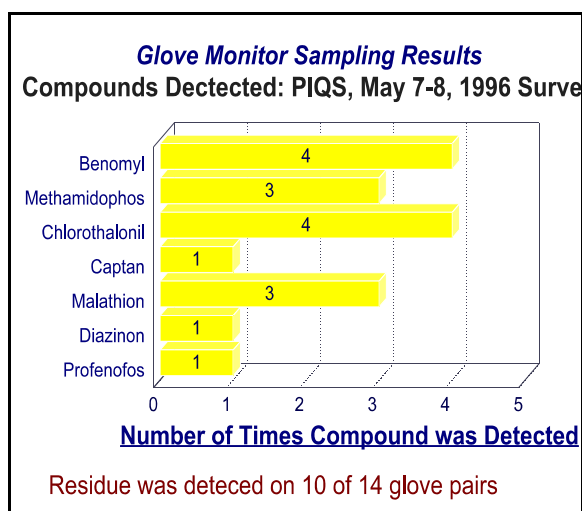


Figure 7

Sixteen sets of glove samples (32 gloves) were collected during this site visit and, based on the results of the wipe sampling, fourteen pairs (28 gloves) were analyzed. The glove samples were analyzed for the compounds detected on the corresponding gauze wipe sample and in some cases for additional compounds. Residue was detected on 10/14 (71%) glove pairs (Figure 7). Note that the analytical LODs varied considerably (e.g., the captan LOD was 80X the benomyl LOD), possibly explaining why some compounds were not detected

on the glove samples. Benomyl and chlorothalonil were the compounds detected most frequently on the glove monitors.

Five area air samples were collected on May 7–8, 1996, including one sample obtained inside the truck bed containing the Dracena (corn plant) from El Salvador. The samples were analyzed for tetradifon, chlorpyrifos, diazinon, malathion, methamidophos, and profenofos. All results were below the LOD for the analytes.

CONCLUSIONS

An evaluation was conducted to assess imported plants for dislodgeable pesticide residues and determine the potential for skin contact and inhalation exposure during the plant inspection process. The results of this evaluation indicate that USDA PIQS plant inspectors are at risk for skin exposure to pesticides while handling imported plants. Pesticide residues were detected on the majority of the foliage samples, and 21 different pesticides were found. Measurable quantities of the pesticides sampled were found on cotton glove monitors worn by plant inspectors. No measurable pesticides were found on any of the air samples. Because of the low volatility of most pesticides, this was not an unexpected finding.

As the cotton glove monitors were worn over the inspectors vinyl or latex glove (when worn), these results only provide information on the potential for exposure if protective gloves were not worn. The efficacy of the disposable gloves to prevent contact with pesticide residues was not evaluated during this project. However, the results of two previous NIOSH HHEs have demonstrated that disposable chemical-resistant gloves can be relied upon to protect a workers' hands from pesticide exposure under certain situations.^(19,20)

The majority of the compounds found on the foliage samples are considered to be highly toxic pesticides, with only one of the detected pesticide in the lowest toxicity ranking. Some of the pesticides detected can present a significant hazard from skin contact and

can be rapidly absorbed. For example, propargite is considered a potent skin and eye irritant, and probable sensitizer. The EPA has recommended that stringent measures be taken to prevent skin contact with such pesticides.⁽¹⁸⁾

This evaluation also showed that the presence of visible residue on plant material was not a good indicator that a pesticide would be detected. Unusual odors were not noted on any of the shipments. PIQS employees were aware of the potential for exposure to residual agricultural chemicals on imported plants and the need to take precautions. However, some employees were observed not wearing gloves during inspections. An inspector's decision to wear gloves during an inspection seemed to be based on the presence of visible residue on the plants, or an unusual odor when a plant container was opened. Although these are prudent measures, pesticide contamination can still be present without odor or visible residue, and the senses should not be used for determining whether precautions should be taken.

RECOMMENDATIONS

A "universal precautions" approach is recommended when handling all imported plants during inspections. This approach entails handling all plant materials as if they were contaminated with pesticide residues. Disposable gloves should always be worn by PIQS inspectors when handling plants. Employees should discard their gloves and thoroughly wash their hands after inspecting plants and prior to consuming food or beverages. Adherence to this policy should be mandatory. These precautions should be incorporated into new employee training requirements.

The USDA should establish regulations requiring exporters to identify shipments of off-shore material that have been treated with pesticides. Periodic testing of plant material for pesticide residue should also be conducted. Exporters should be penalized if pesticides are found on materials that have not been identified as being pesticide contaminated.

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Table 1 USDA Plant Inspection and Quarantine Station Dislodgeable Residue Sampling Results Paired Foliage Punch/Foliage Wipe Sampling June 14, 1995		
<i>Sample Description</i>	<i>Sample #</i>	<i>Compound – micrograms of residue detected</i>
Sanevieria Laurentii from Costa Rica	LP-1	Not Analyzed
	Gauze -1	ND
Orchids from Thailand. Visible residue was present on leaves	LP-2	ND
	Gauze-52	Benomyl, (40)
Orchids from Thailand. Visible residue was present on leaves	LP-3	ND
	Gauze-53	ND
Orchids from Thailand. Visible residue was present on leaves	LP-4	Monocrotophos , 0.37
	Gauze-54	Monocrotophos, 4.3
Orchids from Thailand via Jamaica, no visible residue	LP-5	Aldicarb, (10); Monocrotophos , 0.54
	Gauze-55	Monocrotophos, 8.9
Red Maranta from Costa Rica, visible white residue on leaf edge	LP-6	Benomyl, (20); Chlorothalonil, 8.6
	Gauze-56	Chlorothalonil, 36
Geranium cuttings from Mexico, white residue present, only 3 leaf punches obtained	LP-7	Aldicarb, (10); Carbaryl, (10)
	Gauze-57	ND
Orchids from Thailand – wet when sampled	LP-8	Not Analyzed
	Gauze-58	ND
Orchids from Thailand – wet when sampled	LP-9	ND
	Gauze-59	ND

Note:

LP = Leaf Punch Sample (5 – 1.25 cm² sections per sample)

Gauze Wipes consisted of wiping 5 plant leaves with 3" X 3" gauze moistened with isopropyl alcohol

ND = None Detected

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Table 2 USDA Plant Inspection and Quarantine Station Dislodgeable Residue Sampling Results Paired Foliage Punch/Foliage Wipe Sampling June 15, 1995		
<i>Sample Description</i>	<i>Sample #</i>	<i>Compound –micrograms of residue detected</i>
Bromeliads from Guatemala	LP-10	Aldicarb, (10); Benomyl (10)
	Gauze-60	ND
Bromeliads from Guatemala	LP-11	ND
	Gauze-61	ND
Palm Seeds from Madagascar/Australia	Gauze-62	Chlorothalonil, 0.9
	Gauze-63	ND
Pothos from Jamaica	LP-12	ND
	Gauze-66	ND
Agloenema from Jamaica – visible white residue	LP-13	ND
	Gauze-67	ND

Note:

LP = Leaf Punch Sample (5 – 1.25 cm² sections per sample)

Gauze Wipes consisted of wiping 5 plant leaves with 3" X 3" gauze moistened with isopropyl alcohol

ND = None Detected

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Table 3 USDA Plant Inspection and Quarantine Station Glove Monitoring Results: Aldicarb and Benomyl June 15, 1995						
<i>Sample Description</i>	<i>Sampling Period (min)</i>	<i>Corresponding Foliage Sample</i>	<i>Compound Detected</i>	<i>Concentration</i>		
				<i>hand</i>	<i>µg</i>	<i>µg/hr</i>
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #6	08:50–09:05 (15)	LP–10 Gauze–60	ND	Left	NA	NA
				Right	NA	NA
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #7	08:50–09:07 (17)	LP–10 Gauze–60	Benomyl	Left	(54)	(191)
				Right	(29)	(102)
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #8	08:50–09:08 (18)	LP–10 Gauze–60	Benomyl	Left	66	220
				Right	(40)	(133)
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #9	08:50–09:09 (19)	LP–10 Gauze–60	Benomyl	Left	(46)	(145)
				Right	ND	NA
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #10	08:50–09:11 (21)	LP–10 Gauze–60	Benomyl	Left	(21)	(60)
				Right	(24)	(69)
Inspecting Bromeliads (wild harvest) from Guatemala. Sample #11	08:50–09:12 (22)	LP–10 Gauze–60	Benomyl	Left	(28)	(76)
				Right	110	300

Note:

Sampling glove monitors were worn **over** latex/vinyl glove worn by workers

µg/hr = micrograms of contaminant per hour

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

ND = None Detected, the analytical LOD for benomyl was 20 µg per sample

No Aldicarb was detected on any of the gloves analyzed (LOD = 40µg per sample)

No sampling gloves from June 14, 1995, were analyzed

Table 4 USDA Plant Inspection and Quarantine Station Foliage Sampling (Gauze Wipe) Results May 7, 1996																											
Sample Number and Description	<i>Compounds Detected in Micrograms – see coding key at the bottom of the table for compound identification.</i> Blank space indicates compound was not detected for that sample, X = compound was detected via GC/MS but not quantified																										
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X			
Gauze–43: Orchids from Thailand, Wild Grown						X		X				X		X		X			X	X							
Gauze–44: Orchids from Thailand, Wild Grown	X							X	X			X						X			X						
Gauze–45: Orchids from Thailand, Wild Grown																											
Gauze–46: Orchids from Thailand, Wild Grown						(16)		X								X		X									
Gauze–47: Orchids from Thailand, Wild Grown	X								X									X			X	X	X				
Gauze–48: Orchids from Thailand, Wild Grown	X							X					X														
Gauze–49: Orchids from Thailand, Wild Grown																											
Gauze–50: Orchids from Thailand, Wild Grown																											
Gauze–51: Orchids from Thailand, Wild Grown																											
Gauze–52: Orchids from Thailand, Wild Grown								X				X															
Gauze–53: Orchids from Thailand, Wild Grown								X				X	X										X				
Gauze–54: Corn Plant from El Salvador	X	0.27	0.17			(2,9)		350		(32)					X			X			X						
Gauze–55: Corn Plant from El Salvador		0.73	0.62			(26)		X													X						
Gauze–56: Bottle Grown Orchids from Thailand																											
Gauze–59: Corn Plant from Costa Rica							(22)				(57)				X	8.9									(25)		
Gauze–60: Wipe from truck bed with Corn Plants from El Salvador																4.9											

Table 4 USDA Plant Inspection and Quarantine Station Foliage Sampling (Gauze Wipe) Results May 7, 1996																											
Sample Number and Description	Compounds Detected in Micrograms – see coding key at the bottom of the table for compound identification. Blank space indicates compound was not detected for that sample, X = compound was detected via GC/MS but not quantified																										
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X			
Gauze-61: Orchids from Ecuador (visible residue)																											
Gauze-62: Orchids from Ecuador (visible residue)																											
Gauze-63: Mango seeds from Costa Rica								X																			
Gauze-64: Geraniums from Guatemala															X												
Gauze-69: Blank						X		X											X								
Gauze-57: Blank																											
Gauze-58: Blank																											
Gauze-83: Blank	X														X												

Compound Codes:

A = Chlorothalonil	B = Endosulfan I	C = Endosulfan II	D = Endosulfan Sulfate	E = Endrin-Ketone	F = Benomyl	G = Carbofuran
H = Captan	I = Fluvalinate	J = Metalaxyl	K = Aldicarb	L = Tetradifon	M = Methamidophos	N = Chlorpyrifos
O = Malathion	P = Diazinon	Q = D-Phenthrin	R = Methiocarb	S = Profenophos	T = Propargite	U = Cypermethrin
V = Cyfluthrin	W =	Dodemorph	X = Carbaryl			

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Sample #'s 43,44,45, were from different containers than sample #'s 46-47. Sample #s 49-53 were from a different Grower/Importer.

Shipping paper from sample # 63 indicated commodity was treated with Captan and Subdue (metalaxyl)

Table 5 USDA Plant Inspection and Quarantine Station Foliage Sampling (Gauze Wipe) Results May 8, 1996																										
Sample Number and Description	<i>Compounds Detected in Micrograms</i> – see coding key at the bottom of the table for compound identification. Blank space indicates compound was not detected for that sample, X = compound was detected via GC/MS but not quantified																									
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X		
Gauze–65: Carnations from Jamaica						92			2.4																	
Gauze–66: Carnations/Cut flowers from Costa Rica																										
Gauze–67: Orchids from Thailand (Greenhouse Grown)																										
Gauze–68: Orchids from Thailand (Greenhouse Grown)																										
Gauze–71: Leather Leaf from Columbia	6.1																									
Gauze–72: Cut Flowers/Leather Leaf from Columbia	0.44							X	X	(13)						X		X			X	X				
Gauze–73: Orchids from Belize															760											
Gauze–74: Orchids from Belize															87											
Gauze–75: Orchids from Belize															7.3											

Compound Codes:

A = Chlorothalonil	B = Endosulfan I	C = Endosulfan II	D = Endosulfan Sulfate	E = Endrin-Ketone	F = Benomyl	G = Carbofuran
H = Captan	I = Fluvalinate	J = Metalaxyl	K = Aldicarb	L = Tetradifon	M = Methamidophos	N = Chlorpyrifos
O = Malathion	P = Diazinon	Q = D-Phenthrin	R = Methiocarb	S = Profenophos	T = Propargite	U = Cypermethrin
V = Cyfluthrin	W = Dodemorph	X = Carbaryl				

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Sample #'s 73-75: Shipping papers indicated commodities were treated with malathion

Table 6 USDA Plant Inspection and Quarantine Station Glove Monitoring Results May 7, 1996								
#	Sample Description	Sampling Period (min)	Corresponding Foliage Sample	Compounds Detected	Concentration Detected			
					Right,		Left	
					µg	µg/hr	µg	µg/hr
118	Inspecting wild grown orchids from Thailand, no visible residue present	08:50–09:25 (35)	Gauze 43–44	Benomyl	(11)	(18.9)	(11)	(18.9)
				Methamidophos	77*	132*	100*	171.4*
				Chlorothalonil	(0.048)	(0.08)	(0.043)	(0.07)
116	Inspecting wild grown orchids from Thailand, no visible residue present	08:51–09:17 (26)	Gauze 45–46	Benomyl	(101)	(233)	ND	
				Methamidophos	30*	69*	ND	
117	Inspecting wild grown orchids from Thailand, no visible residue present	08:52–09:22 (30)	Gauze 44–45	Methamidiopos	120*	240*	130*	260*
121	Inspecting orchids from Thailand, different Broker than Gauze 43–46, visible residue present.	09:42–10:01 (19)	Gauze 50	ND				
120	Inspecting orchids from Thailand, different Broker than Gauze 43–46, visible residue present.	09:42–10:01 (19)	Gauze 51	Chlorothalonil	(0.042)	(0.13)	ND	
119	Inspecting orchids from Thailand, different Broker than Gauze 43–46, visible residue.	09:45–0:958 (13)	Gauze 49	ND				
122	Inspecting orchids from Ecuador, odor/residue present	11:20–11:40 (20)	Gauze 61	ND				
123	Inspecting orchids from Ecuador, odor/residue present	11:20–11:40 (20)	Gauze 62	ND				
124	Inspecting Mango Seeds from Costa Rica, wet. Shipping paper indicated treatment with Captan and Subdue® (metalaxyl)	13:19–13:24 (5)	Gauze 63	Benomyl	(49.3)	(5916)	(52.7)	(632.4)
				Captan	(778)	(9336)	1740	20,880
				Malathion	11	132	28	336
				Diazinon	ND		(5)	(60)
				Profenofos	(4)	(48)	ND	
125	Inspecting Geraniums from Guatemala	15:12–15:22 (10)	Gauze 64	Chlorothalonil	0.66	3.96	(0.12)	(0.72)
				Endosulfan Sulfate	0.39	2.34	(0.076)	(0.46)

Note: Sampling glove monitors were worn **over** latex/vinyl glove worn by workers

µg/hr = micrograms of contaminant per hour

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

ND = None Detected

* = Results are semi-quantitative only

The glove samples were analyzed for the compound detected on the corresponding foliage samples, and in some cases (organophosphate pesticides) for additional compounds. **Not all glove samples were analyzed for all compounds.** LOD/LOQs for the compounds are as follows:

<i>Compound</i>	<i>LOD (µg/glove)</i>	<i>LOQ (µg/glove)</i>
Chlorpyrifos	2	6.6
Diazinon	5	15
Malathion	2	6.6
Methamidophos	10	46
Profenofos	4	11
Aldicarb	60	200
Benomyl ¹	10	33
Captan	800	2700
Bifenthrin ⁴	20	72
Carbaryl	20	78
Oxamyl ⁴	80	280
Carbofuran	10	43
Fluvalinate ²	200	670
Fluvalinate ³	0.8	2.7
Metalaxyl	90	290
Methiocarb	70	230
d-Phenothrin ^{2,4}	100	390
d-Phenothrin ^{3,4}	80	260
Chlorothalonil	0.04	0.13
Endosulfan I	0.04	0.13
Endosulfan II	0.04	0.13
Endosulfan Sulfate ⁴	0.04	0.13
Endrin Ketone ⁴	0.04	0.13
Tetradifon	0.2	0.66
Cyfluthrin	2	3.8
Cypermethrin	1	2.1
Dodemorph	20	81
Propargite	30	110

Footnotes

1 = As carbendazim (breakdown product)

2 = HPLC/UV analytical method

3 = GC/ECD analytical method

4 = Not detected on any PIQS samples

Table 7 USDA Plant Inspection and Quarantine Station Glove Monitoring Results May 8, 1996								
#	Sample Description	Sampling Period (min)	Corresponding Foliage Sample	Compounds Detected	Concentration Detected			
					Right		Left	
					µg	µg/hr	µg	µg/hr
126	Inspecting carnations/cut flowers from Jamaica for re-export to Costa Rica	09:23–09:37 (14)	Gauze 63.64	Benomyl	60	257	(27)	(116)
131	Inspecting cut flowers/leather leaf from Columbia	13:24–13:33 (9)	Gauze 71,72	Chlorothalonil	ND		5	33
111	Inspecting orchids from Belize, wild grown, malathion had been applied, visible residue present	13:51–14:18 (27)	Gauze 73–75	Malathion	42	93	570	1267
132	Inspecting orchids from Belize, wild grown, malathion had been applied, visible residue present	13:51–14:10 (19)	Gauze 73–75	Malathion	1100	3474	1000	3158

Note: Sampling glove monitors were worn **over** latex/vinyl glove worn by workers

µg/hr = micrograms of contaminant per hour

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

ND = None Detected

* = Results are semi-quantitative only

The glove samples were analyzed for the compound detected on the corresponding foliage (gauze) samples, and in some cases for additional compounds. **Not all glove samples were analyzed for all compounds.** LOD/LOQs for the compounds are as follows:

<i>Compound</i>	<i>LOD (µg/glove)</i>	<i>LOQ (µg/glove)</i>
Chlorpyrifos	2	6.6
Diazinon	5	15
Malathion	2	6.6
Methamidophos	10	46
Profenofos	4	11
Aldicarb	60	200
Benomyl ¹	10	33
Captan	800	2700
Bifenthrin ⁴	20	72
Carbaryl	20	78
Oxamyl ⁴	80	280
Carbofuran	10	43
Fluvalinate ²	200	670
Fluvalinate ³	0.8	2.7
Metalaxyl	90	290
Methiocarb	70	230
d-Phenothrin ^{2,4}	100	390
d-Phenothrin ^{3,4}	80	260
Chlorothalonil	0.04	0.13
Endosulfan I	0.04	0.13
Endosulfan II	0.04	0.13
Endosulfan Sulfate ⁴	0.04	0.13
Endrin Ketone ⁴	0.04	0.13
Tetradifon	0.2	0.66
Cyfluthrin	2	3.8
Cypermethrin	1	2.1
Dodemorph	20	81
Propargite	30	110

Footnotes

1 = as carbendazim (breakdown product)

2 = HPLC/UV analytical method

3 = GC/ECD analytical method

4 = Not detected on any PIQS samples

Table 8 USDA Plant Inspection and Quarantine Station Information on Compounds Detected on Imported Plants							
Compound Detected	Pesticide Action	EPA Toxicity Classification**	Compound Classification				
			Organo-phosphate	Carbamate	Pyrethroid	Organo-chlorine	Other ¹⁸
Chlorpyrifos	Insecticide	II	X				
Diazinon	Insecticide/Nematicide	II or III	X				
Malathion	Insecticide	III	X				
Methamidophos	Insecticide/Acaricide	I	X				
Profenofos	Insecticide/Acaricide	II	X				
Chlorothalonil	Fungicide	I				X	
Metalaxyl	Fungicide	III					Organic Fungicide
Captan	Fungicide	I					Thiophthalimide
Carbaryl	Insecticide	I		X			
Carbofuran	Insecticide/Nematicide	I		X			
Methiocarb	Insecticide/Acaricide/Molluscicide	I		X			
Aldicarb	Insecticide/Acaricide/Nematicide	I		X			
Tetradifon	Acaricide	III				X	
Dodemorph**	Fungicide	II					Organic Fungicide
Propargite	Acaricide	I					Sulfite Ester
Benomyl	Fungicide	IV					Benzimidazole
Cypermethrin	Insecticide	II			X		
Cyfluthrin	Insecticide	II or I (eye)			X		
Fluvalinate	Insecticide	I			X		
Endosulfan	Insecticide/Acaricide	I				X	

** Dodemorph manufacture has been discontinued. Dodemorph acetate is available

* The EPA has established toxicity categories for pesticides based on oral, inhalation, and dermal toxicity, and eye and skin effects. The categories range from I (highly toxic) to IV (least toxic). These toxicity designations dictate the necessary hazard warnings on pesticide labels (e.g., danger, warning, caution, etc.). Classifications for the same compound may vary depending on the formulation.

Appendix A

Dislodgeable Residue and Glove Monitor Sampling

Assessing the presence of unknown pesticide residues on foliar surfaces presented a significant analytical challenge. Pesticide chemistry is complex because there are many types of pesticides in numerous chemical classes and no single analytical method is available to assess a sample for “all” potential pesticides. As such, the sampling and analytical method(s) conducive to measuring the largest number of pesticides potentially present at a reasonable sensitivity had to be determined. Methods for sampling dislodgeable pesticide residue from leaf surfaces have been previously developed and generally consist of leaf punch, whole leaf, or leaf wipe sampling.^(1,2) Measuring dislodgeable residue is useful for worker exposure assessments (estimation of the amount of dislodgeable pesticide residue that could be transferred to workers) and for the establishment of re-entry intervals.^(3,4,5,6) Studies investigating the relationship between dislodgeable foliar residue and skin exposure have been conducted and in some cases transfer factors (from leaves to hands) have been calculated.^(4,7) The most widely referenced foliar sampling technique entails the collection of a known surface area of leaves using a leaf punch into a collection jar containing a surfactant. Most dislodgeable foliar residue studies, however, have focused on measuring only a small number of pesticides that were known to have been applied, as opposed to the assessment of a large number of unknown contaminants. The advantage of the leaf punch method is that the area sampled is easily measured and standardized, and residue measurements can be reported in a mass of contaminant per leaf area unit. This allows for ready comparison with other samples. In general, the surface area sampled can only be approximated when using the wipe sampling method.

During the February 1995 field trial, dislodgeable residue samples were collected from ornamental plants at a greenhouse with a documented history of pesticide applications (volume, date, application method). Several classes of pesticides had recently been applied (organochlorine, organophosphate, and pyrethroid), ranging from over 1 month to a few days prior to sample collection. For each trial, samples were collected from each plant (when possible) or an adjacent plant, that consisted of the following sample set:

Pre-extracted 3" X 3" cotton gauze

1. One leaf wiped (both sides) using commercially available 70% isopropyl alcohol
2. 10 leaves wiped (both sides) using commercially available 70% isopropyl alcohol
3. One leaf wiped (both sides) using technical-grade 99% isopropyl alcohol
4. 10 leaves wiped (both sides) using technical-grade 99% isopropyl alcohol

Leaf Tissue Sampling

1. One 5 cm² leaf punch
2. Ten 5 cm² leaf punches

The leaf samples were obtained using a Birkestrand Precision Sampler Punch that allows the sample jar to be attached directly to the punch as previously described. No surfactant or solution was added to the leaf punch samples. The punch cutting area was cleaned between sample collections.

For each sample, the plant type, country of origin, presence of any visible residue or odor, and any shipping notations of pesticide applications were recorded. Samples were placed in labeled amber jars and stored in a freezer prior to shipment, and were shipped cold via overnight express to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis.

The results of this trial indicated the gauze wipe technique was more sensitive than the leaf punch method. It was not determined if this was due to removal efficiency, unequivalent surface area sampled, or analytical sensitivity (the LODs for the leaf punch samples were higher than the gauze samples). Although there did not seem to be much difference between the commercially available isopropyl alcohol (IPA) and the technical grade IPA, the use of technical grade IPA did have certain advantages. For instance, compounds that are particularly water soluble would be difficult to extract from 70% IPA, and the 99% IPA would dilute well with almost any other organic solvent used in the analysis and would increase the options available to the chemist. Additionally, this trial showed that wiping ten leaves instead of one leaf significantly improved the chance of detecting residue.

Based on this field evaluation, and the HHE objectives (detecting residue was more important than quantification), the gauze wipe technique using 3" X 3" pre-extracted cotton gauze moistened with technical grade IPA and wiping both sides of 5 leaves was determined to be the optimum method for this project.

Analytical Methods Summary: June 14–15, 1995, Survey

Gauze Sampling

All gauze wipe samples were desorbed with 20 ml. IPA and one-hour of continuous agitation. Aliquots from each sample were analyzed by three separate techniques. This was necessary to measure the various pesticide classes.

1. Organochlorine pesticide screen using gas chromatography with electron capture detection.
2. Organo-phosphate pesticide screen via NIOSH method 5600 (modified) using gas chromatography with flame photometric detection.
3. Carbamate and urea pesticides using high performance liquid chromatography with ultraviolet absorbance detection (variable wavelength).

Media blanks and media spikes were prepared by the same techniques used for preparing the samples. For the media spikes, liquid standards were used to spike the gauze samples at various concentrations and the average recoveries were determined.

Leaf Sampling

All leaf samples were desorbed with 10 ml. IPA and one-hour of continuous agitation. Aliquots from each sample were analyzed by the same three techniques used for the gauze samples. Media spikes were prepared by spiking leaves with known concentrations and sample recoveries for each analyte were determined.

Compounds Measured on Foliage Samples: June 14–15, 1995, Survey. (LOD and LOQ units are micrograms per sample):

<u>Compound</u>	<u>Gauze</u>		<u>Leaf</u>	
	<u>LOD</u>	<u>LOQ</u>	<u>LOD</u>	<u>LOQ</u>
Aldicarb	20	68	10	33
Benomyl	20	67	10	33
Carbaryl	20	67	10	33

<u>Compound</u>	Gauze		Leaf	
	<u>LOD</u>	<u>LOQ</u>	<u>LOD</u>	<u>LOQ</u>
Carbofuran	20	67	10	33
Oxamyl	20	67	10	33
Fluvalinate	30	100	10	33
Bifenthrin	20	67	10	33
Azinphos Methyl	2	6.4	1	3.2
Bolstar	0.3	0.84	0.1	0.42
Chlorpyrifos	0.2	0.57	0.09	0.29
Coumaphos	1	4.2	0.6	2.1
Demeton O and S	0.5	1.7	0.2	0.8
Diazinon	0.5	1.6	0.2	0.79
Dichlorvos	0.1	0.43	0.06	0.22
Dimethoate	1	4.4	0.6	2.2
Disulfoton	0.3	0.88	0.1	0.44
EPN	0.9	2.9	0.4	1.5
Ethoprop	0.5	1.6	0.3	0.9
Fenamiphos	0.1	0.49	0.07	0.25
Fensulfothion	0.8	2.5	0.4	1.3
Fenthion	0.9	3.0	0.4	1.5
Malathion	0.2	0.66	0.1	0.33
Merphos	0.6	2.2	0.3	1.1
Mevinphos	0.6	2.1	0.3	1.1
Monocrotophos	0.2	0.52	0.08	0.26
Naled	1.0	4.8	0.7	2.4
Parathion	0.6	2.0	0.3	1.0
Parathion Methyl	0.6	2.0	0.3	0.99
Phorate	0.6	2.0	0.3	1.0
Ronnel	0.2	0.65	0.1	0.33
Sulfotep	0.1	0.44	0.07	0.22
Stirophos	0.8	2.6	0.4	1.3
TEPP	2	4.8	0.8	2.4
TPP	0.4	1.4	0.2	0.7
Tokuthion	0.1	0.42	0.06	0.21
Trichloronate	0.7	0.25	0.4	1.3
Aldrin	0.1	0.33	0.05	0.17
Alpha-BHC	0.1	0.39	0.06	0.20
Beta-BHC	0.1	0.35	0.05	0.18
Delta-BHC	0.1	0.39	0.06	0.20
Lindane	0.1	0.35	0.05	0.18
Alpha-Chlordane	0.1	0.36	0.05	0.18
Gamma-Chlordane	0.1	0.32	0.05	0.16
4,4' – DDD	0.1	0.32	0.05	0.16
4,4' – DDE	0.1	0.37	0.06	0.18
4,4' – DDT	0.1	0.39	0.06	0.19
Dieldrin	0.1	0.39	0.05	0.16
Endosulfan I	0.1	0.29	0.04	0.15
Endosulfan II	0.1	0.30	0.05	0.15
Endosulfan Sulfate	0.1	0.20	0.03	0.11
Endrin	0.1	0.39	0.06	0.19
Endrin Aldehyde	0.1	0.22	0.03	0.11
Heptachlor	0.1	0.36	0.05	0.18
Heptachlor Epoxide	0.1	0.25	0.05	0.15
Methoxychlor	0.1	0.25	0.04	0.12
Mirex	0.01	0.046	0.01	0.023
Chlorothalonil	0.06	0.19	0.03	0.095

<u>Compound</u>	Gauze		Leaf	
	<u>LOD</u>	<u>LOQ</u>	<u>LOD</u>	<u>LOQ</u>
Endrin Ketone	0.06	0.19	0.03	0.096
Toxaphene	NA	NA	NA	NA

NOTE: Toxaphene is a multi-component analyte which is identified by a specific pattern and quantified by summation of the most prominent peaks. Therefore, only one standard for Toxaphene was prepared to screen the samples and an LOD and LOQ could not be calculated.

Glove Samples

Pre-extracted 100% cotton “inspectors” gloves were used to assess worker potential for hand contact with pesticides. The gloves were analyzed for corresponding compounds detected on the foliage samples. For the June 14–15, 1995, survey, the glove samples were analyzed for aldicarb and benomyl. Each sample was first sonicated for 60 minutes in a buffered acetonitrile solution. The solution was then filtered and analyzed using high performance liquid chromatography with an ultraviolet detector (220 nanometers wavelength). Liquid standards were prepared by diluting an aliquot of stock solution. Media QC samples were prepared and analyzed in the same manner as the field samples.

Analytical Methods Summary: May 7–8, 1996, Survey

Gauze Sampling

All gauze wipe samples were left in their shipping bottle and desorbed with 25 ml. IPA. Each sample was then tumbled from 4 (carbamates) to 8 (organochlorine and organo-phosphate) hours. As with the June 1995 samples, aliquots from each sample were analyzed by three separate techniques.

1. Organochlorine pesticide screen using gas chromatography with electron capture detection.
2. Organo-phosphate pesticide screen via NIOSH method 5600 (modified) using gas chromatography with flame photometric detection.
3. Carbamate and selected pyrethroid pesticides, captan and metalaxyl using high performance liquid chromatography with ultraviolet absorbance detection (variable wavelength).

The samples were analyzed for the same compounds measured in the June 1995 survey plus the fungicides captan and metalaxyl. A different gauze type (polyester) and manufacturer (NuGauze®) was used. Laboratory desorption efficiencies were determined using samples spiked with known liquid standards and this gauze was determined to provide better recoveries. As such, some of the LODs and LOQs for the analytes were different than those noted from the June 1995 survey. The LODs and LOQs for captan and metalaxyl were, in micrograms, 100, 430, and 10, 42, respectively.

Media blanks and media spikes were prepared by the same techniques used for preparing the samples. For the media spikes, liquid standards were used to spike the gauze samples at various concentrations and the average recoveries were determined.

Additional compounds were suspected to be present on some of the samples and a separate aliquot from these samples was further analyzed by gas chromatography/mass spectroscopy (GC/MS).

Glove Samples

Quality control studies indicated that pre-extracted 65%/35% polyester/cotton glove monitors would provide better recoveries and gloves made of this material were used for the May 1996 survey. At the laboratory, the gloves were left in their shipping bottle and desorbed with 40 ml. of technical grade IPA. The samples were then tumbled for 3 hours and refrigerated at 0–4° C until needed. The samples were analyzed for the compounds detected on the corresponding gauze sample, and in some cases for additional compounds. Analysis was similar to that used for the gauze samples.

1. Organochlorine pesticide screen using gas chromatography with electron capture detection.
2. Organo-phosphate pesticide screen via NIOSH method 5600 (modified) using gas chromatography with flame photometric detection.
3. Carbamate and selected pyrethroid pesticides, captan and metalaxyl using high performance liquid chromatography with ultraviolet absorbance detection (variable wavelength).
4. Dodemorph and Propargite using GC/MS via EPA method 8270 for semivolatiles.

Media samples were prepared by spiking new gloves with known concentrations and analyzing them in duplicate, along with the samples and media blanks. Desorption efficiencies were determined.

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Appendix B

USDA HETA 94-0353 Pesticide List

Possible compounds applied to imported commodities

<u>Pesticide</u>	<u>Compound Class</u>	<u>Reason for Selection</u>
Aldicarb (Temik®)	Carbamate	1,2,3
Mirex	Organo-chlorine	1,2
Lindane	Organo-chlorine	1,2
Endosulfan	Organo-chlorine	1,2,3
Benomyl (Benlate®)	Benzimidazole	1
Carbaryl (Sevin®)	Carbamate	1,3
Carbofuran	Carbamate	1,2
Chlorothalonil (Daconil®)	Substituted Benzene	1,3
Oxamyl (Vydate®)	Carbamate	1,2,3
Fenamiphos	Organo-phosphate	1,2,3
Diazinon	Organo-phosphate	3
Dimethoate (Cygon®)	Organo-phosphate	3
Fluvalinate (Mavrik®)	Pyrethroid	2,3
Chlorpyrifos (Dursban®)	Organo-phosphate	3
Bifenthrin (Talstar®)	Pyrethroid	3

NOTE

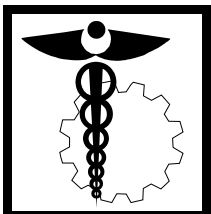
1 = Pesticide was a high-volume import into a Central-American Country

Duszeln, J [1991]. Pesticide contamination and pesticide control in developing countries: costa rica, central america. In: Richardson, M, ed. Chemistry, Agriculture and the Environment. RSC.

2 = Pesticide is considered to have a high order of toxicity (EPA Toxicity Classification I).

3 = Pesticide is recommended for use in the ornamental plant industry.

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